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Thiophenes as Traps for Benzyne. 3. Diaryl Sulfides and the Role of Dipolar Intermediates†

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Received October 3, 2002

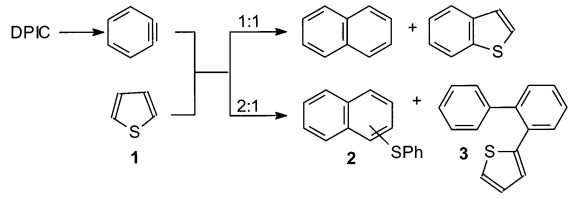
The reactions of seven thiophenes with benzyne generated from diphenyliodonium-2-carboxylate (DPIC) under a standard set of conditions led among other products to the formation of α- and *β*-naphthyl phenyl sulfides **2a** and **2b** from thiophene (**1a**) and of **2c** and **2d** from 2-methylthiophene (**1b**). Dithienyl sulfides **4a**−**f** were produced from the halothiophenes **1c**−**g**. The structures of the naphthyl sulfides were proven by comparison with authentic samples of **2a**−**f**, thus eliminating one of two possible mechanisms of formation. The remaining mechanism involves [4+2]-cycloaddition of benzyne to thiophene or to an *S*-phenylthiophenium ylide **10** to give the dipolar 2:1 benzyne/thiophene adduct **8** followed by ring-opening. Stevens-like rearrangements of **11**, formed from **10** by proton transfer, may also explain the origin of arylated thiophenes such as **12** and **3** found in some reactions of benzynes with thiophene.

Introduction

Thiophene is generally considered to be an indifferent partner in thermal cycloaddition reactions,[1] presumably because of its considerable aromatic character compared to the other five-membered heterocycles, furan and pyrrole. Exceptions include strongly electron-deficient dienophiles such as benzyne,[2] 1,2-dehydro-*o*-carborane,[3,4] and 2,3-didehydrothiophene.[5] The last of these is particularly interesting in that a study with appropriately substituted thiophenes revealed that [2+2]-cycloaddition actually predominated over the usual [4+2] pathway.[6] It was suggested that the reasons for this unusual behavior were due to either the reaction conditions [flash vacuum thermolysis],[7] the diradical or dipolar character of the "thiophyne", or a greater tendency of thiophene than other dienes to undergo [2+2]-cycloaddition reactions.[1] To test this last possibility, the study of the reactions of benzyne with thiophene was undertaken.

The efficiency of benzyne as a reaction partner depends on the use of benzyne precursors and conditions that minimize precursor side reactions with themselves or with thiophene.[2] Diphenyliodonium-2-carboxylate [DPIC] at 180 °C was the best of several tested in this regard.[8]

Products involving 1:1 reactions of thiophene (**1**) with benzyne consisted of naphthalene and benzo[*b*]thiophene. Studies with alkyl-substituted thiophenes revealed that the former compound arose by [4+2]- and, to a lesser extent, [2+2]-cycloaddition,[9] while the latter was formed via an unusual [3+2]-cycloaddition.[10] With the alkyl thiophenes, ene and double-ene products were also observed.[9] The remaining products, α- and *β*-naphthyl phenyl sulfides (**2**) and *o*-(2-thienyl)biphenyl (**3**), apparently involve a 2:1 reaction of benzyne and thiophene. This paper reports the reactions of seven thiophenes (**1a**−**g**) with DPIC, which permit a rationalization of these products by a mechanism that provides insight into the role of polar intermediates in the reaction of thiophenes with benzyne.



eq. 1

Results

Two types of diaryl sulfides were found in the reactions of DPIC-generated benzyne with substituted thiophenes (Table 1): (i) naphthyl phenyl sulfides [**2a** and **2b** from thiophene (**1a**) and **2c** and **2d** from 2-methylthiophene (**1b**)] and (ii) dithienyl sulfides (**4**) from the halothiophenes

† Dedicated to Professor Henry Rapoport ["Rap"] 1918−2002.

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10.1021/jo0265176 CCC: $25.00
Published on Web 11/15/2002

TABLE 1. Naphthyl Phenyl (2) and Dithienyl (4) Sulfides from Thiophenes (1) and Benzyne

thiophene	phenyl (**2**) and dithienyl[a] (**4**) sulfides (% yield)
H (**1a**)	1-naphthyl (**2a**) (9);[b] 2-naphthyl(**2b**) (6)[b]
2-Me (**1b**)	1-methyl-4-naphthyl (**2c**) (2);[b,c] 1-methyl-3-naphthyl-**2d** (1)[c]
2-Br (**1c**)	Th_2S (**4a**) (10)[d]
3-Br (**1d**)	Th_2S (**4a**) (4.7);[d] Th_2S (**4b**) (1.3)[d]
2,5-Br_2 (**1e**)	Th_2Br_2S (**4c**) (tr.)
3,4-Br_2 (**1f**)	$(3\text{-Br-4-Th})_2S$ (**4d**) (1.5)
2,5-Cl_2 (**1g**)	Th_2Cl_2S (**4e**) (4); Th_2Cl_3S (**4f**)

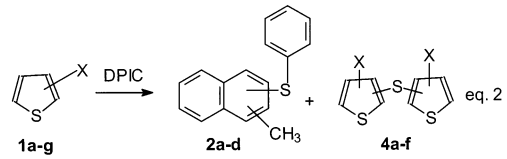
[a] Unless otherwise noted, the structures (or partial structures) are based on MS-determined M^+ and heteroatom content (isotope abundance, Table 2). [b] Identified by GC/MS comparison with an authentic sample. [c] The relative retention times of **2c**, **2d**, and an authentic sample of 2-methyl-1-naphthyl phenyl sulfide (**2e**) were 1.00, 1.08, and 0.79 ± 0.01, respectively, under several sets of GC conditions. [d] GC/MS retention times of **4a** and **4b** are 3:58 and 4:12 min at 130−220° at 9°/min.

TABLE 2. Mass Spectra of Dithienyl Sulfides 4[a]

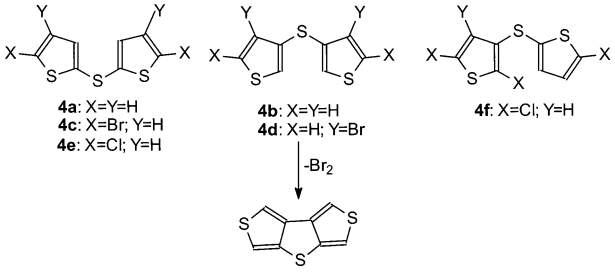
ion	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**
M+4			14(13)	10(10)	11(11)	20(21)
M+2	12	12	23(21)	16(17)	47(47)	51(49)
M	100	100	10	8	59	44
M−SH	22	29				
M−CHS	34	40				
M−X			40	3	100	100
M−2X			85	100	58	76
M−CSX			6		35	
$M-C_4H_2SX_2$			100	6		
$M-CHS_2$	19	24				
$C_4HS_2Cl_2$					0	10
$C_4H_2S_2Cl$					13	11
C_3H_2SCl					47	33
C_4H_2S			61	10		
C_3H_3S	28	41				
C_3HS			88	14	49	64

[a] Relative intensities (calculated value based on assigned formula); X = halogen.

(**1c**−**g**). The structures of the naphthyl phenyl sulfides (**2a**−**d**) were determined by GC/MS comparisons with authentic samples that also included 2-methyl-1-naphthyl (**2e**) and 1-methyl-2-naphthyl phenyl sulfides (**2f**) as possible products on the basis of mechanistic considerations (cf. Discussion).



All of the halothiophenes formed at least one dithienyl sulfide **4**, but only partial structures were assigned on the basis of mass spectra (Table 2). The probable structures are those expected from substitution at the halogen-bearing carbons based on the known formation of dithienyl sulfides **4** by the reaction of halothiophenes with H_2S or thiophenethiols.[11] Both are known products of the reactions of benzyne or sulfur with thiophene.[12] However, the fact that 3-bromothiophene (**1d**) gives two sulfides, one of which (**4a**) is identical to the one produced from 2-bromothiophene (**1c**), indicates that some rearrangement must be taking place. Furthermore, the formation of a trichlorodithienyl sulfide **4f** from 2,5-dichlorothiophene (**1g**) suggests that substitution at a non-halogen-bearing carbon also can occur. Accordingly, the assigned structures for the sulfides **4** must be considered tentative except perhaps for **4d**, where the base peak loss of Br_2 provides especially good support for the structure shown.



Discussion

The origin of the naphthyl sulfides **2** is neither obvious nor trivial, accounting for 15% of the product from thiophene itself. Two mechanisms have literature precedent. The first is analogous to that proposed for the formation of phenyl vinyl sulfide from 3-pyrrolidinylthiophenes and dimethyl acetylenedicarboxylate (DMAD).[13] This mechanism involves the [2+2]-cycloaddition of benzyne to either side of the thiophene, ring-opening to a thiepin, ring-closure to thianorcaradiene **5**, and reaction with a second molecule of benzyne at sulfur to give betaines **6**, which ring-open to the naphthyl phenyl sulfides **2** (Scheme 1). This mechanism explains the formation of sulfides **2a** and **2b** from thiophene (Scheme 1, R = H), but not for the 1-methyl-4-naphthyl (**2c**) and 1-methyl-3-naphthyl (**2d**) isomers from 2-methylthiophene (**1b**) (Scheme 1, R = Me). Instead, the predicted phenyl sulfides would be the 1-methyl-2-naphthyl (**2f**) and 2-methyl-1-naphthyl (**2e**) isomers, which are not found (Table 1).

The second mechanism is analogous to ones proposed for the reactions of benzynes with pyrroles[14] to give dihydrocarbazoles,[15] naphthalenes,[16] and α-naphthylamines.[17] This mechanism involves [4+2]-cycloaddition of benzyne to thiophene to give **7**, addition of a second molecule of benzyne to give the betaine **8**, ring-opening of the 1,4-sulfur bridge of **8** to the more stable 3° allylic cation, and, finally, proton transfer to give the α-naphthyl phenyl sulfides **2a** and **2c** (Scheme 2, R = H and Me). Alternatively, a [1,5]-sigmatropic shift of the 1,4-sulfur bridge of **8** would give a betaine **9** identical to **6** in Scheme 1 except for the relative position of the substituent. In this case ring-opening leads to the *β*-naphthyl sulfides **2b** from thiophene and **2d** from 2-methylthiophene, as observed.

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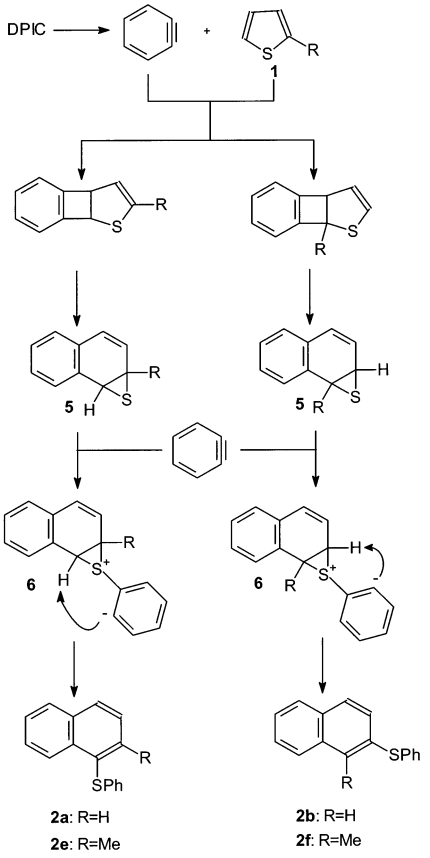
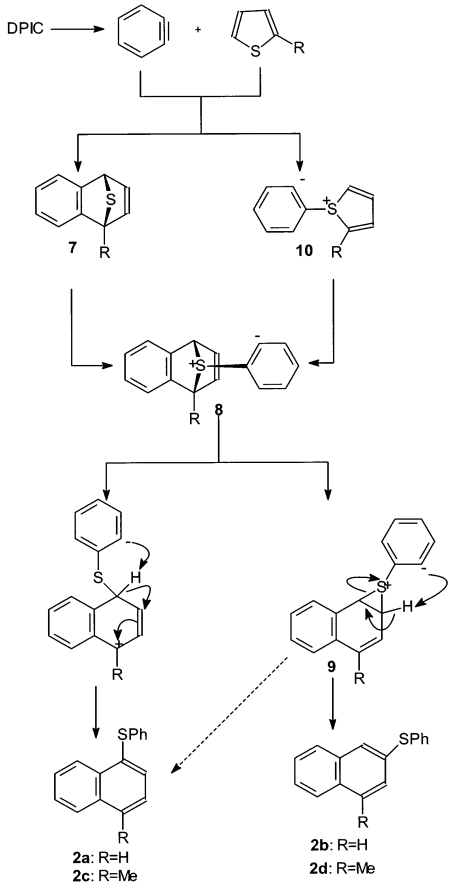
SCHEME 1



SCHEME 2



Thus, both the 1:1[9] and the 2:1 reactions of benzyne with thiophenes proceed primarily by [4+2]- rather than by [2+2]-cycloadditions. The converse behavior of 2,3-didehydrothiophene[6] must therefore be due to its diradical or dipolar character, consistent with a recent *ab initio* study.[18]

Role of Dipolar Species in the Reactions of Benzyne and Thiophene. The precedents cited above for the formation of betaines similar to **6** and **8** all involve reactions in which at least one of the reaction partners, the alkyne (DMAD) or the heterocyclic intermediates (nitrogen analogues of **5** and **7**), are relatively stable molecules and hence present in significant concentration. On the contrary, formation of betaines **6** and **8** requires the unlikely trapping of one low-concentration reactive intermediate (benzyne) with another (thianorcaradiene **5** or 1,4-thiacyclohexadiene **7**). This objection could be overcome if the order of benzyne attack was reversed so that it occurred first on the sulfur atom and then on the π-system of the thiophenes present in large excess as the reaction solvent. The resulting betaine **8** has been implicated in the formation of the benzo[*b*]thiophenes[10] and is analogous to intermediates proposed in reactions of benzyne with a variety of other sulfur compounds[19,20] including alkyl aryl sulfides,[21] dialkyl sulfides,[22] thiiranes,[23] 1,3-dithiolanes,[24] and 2,5-dihydrothiophenes.[25] Certain thiophenes do form stable S,C-ylides[26] and *S*-thiophenium salts,[27] but no verifiable examples of their behavior as dienes in [4+2]-cycloaddition have been published. While both semiempirical[28] and *ab initio* calculations[29] predict strong diene reactivity for the *S*-methylthiophenium ion, promised experimental details of a claimed success[29] have yet to appear. The related thiophene *S*,*N*-ylides,[30] oxides, and dioxides,[31] however, do display substantial diene reactivity. In the case of **10** [4+2]-cycloaddition by a second molecule of benzyne would give the betaine **8**, thus accounting for the products in Scheme 2.

Alternatively, **10** might first rearrange to the more stable isomeric ylide **11**, which, based on the increased

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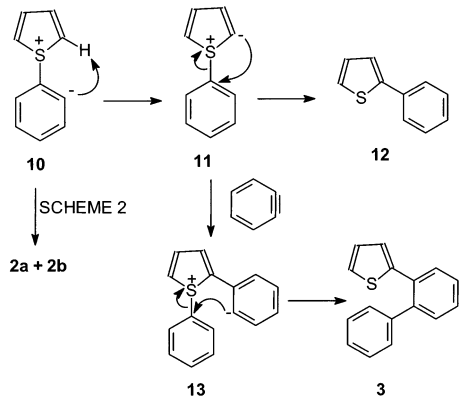
SCHEME 3



reactivity of aryl anions in Diels−Alder reactions with benzyne,[32] may be a more reactive diene component in the [4+2]-cycloaddition. The rearrangement of **10** to **11** would be driven by the increased stability of α-thienyl anions[33] and finds analogy in the reactions of other benzyne-sulfur betaines.[25] The intermediacy of ylide **11** permits mechanistic rationalizations of the formation of 2-phenylthiophenes (**12**)[8,34] and *o*-(2-thienyl)biphenyl (**3**)[8] in the reactions of benzynes with thiophene. Both mechanisms involve a Stevens[35] or similar[36] rearrangement, the former directly on ylide **11** and the latter on betaine **13** produced by the addition of a second molecule of benzyne to **11**.

Experimental Section

General Methods. Analytical instrumentation and methods as well as standard conditions for the reactions of the thiophenes with DPIC are described in detail in an earlier paper in this series.[9]

Materials. The following known reactants or authentic samples were synthesized by the cited literature procedures, or where modified procedures were used, the physical and spectral properties (mp, NMR, MS) were identical to the indicated literature values or were consistent with the assigned structures: diphenyliodonium-2-carboxylate (DPIC),[37] 1-naphthyl phenyl sulfide (**2a**),[38] 2-naphthyl phenyl sulfide (**2b**),[39] 2-methyl-1-naphthyl phenyl sulfide (**2e**).[40] All other known compounds were commercially available.

4-Methyl-1-naphthyl phenyl sulfide (**2c**) was prepared by adding a solution of 1.00 g (4.5 mmol) of 1-bromo-4-methylnaphthalene in 5 mL of dry DMSO to a refluxing solution of 990 mg (9.0 mmol) of thiophenol and 490 mg (9.0 mmol) of commercial sodium methoxide in 5 mL of DMSO. After heating at reflux for 35 h, the reaction mixture was cooled, diluted with ether, washed with 10% NaOH and water, and dried. Evaporation of the solvent left a thick oil, which was passed through a 15 g silica gel column with hexane as the eluent to give 300 mg (27%) of the product **2c** as a colorless oil: ^{1}H NMR 8.22(m,1H), 7.75(m,1H), 7.32(m,3H), 6.96(m,6H), 2.48(s,3H); ^{13}C NMR 137.9, 136.2, 133.8, 133.4, 128.9, 128.2, 127.9, 126.6, 126.4, 126.2, 125.5, 124.7, 19.6; MS 252(6), 251(20), 250(100), 249(17), 235(25), 234(31), 217(14), 215(12), 202(16), 171(7), 141(18), 139(12), 129(10), 128(14), 117(11), 115(19); IR 3060, 1585, 1475, 1440, 1375, 1010, 810, 720. Anal. Calcd for $C_{17}H_{14}S$: C, 81.6; H, 5.6. Found: C, 81.5; H, 5.7.

1-methyl-3-naphthyl phenyl sulfide (2d) was prepared as described below for **2f** from 1.0 g (4.5 mmol) of 3-bromo-1-methylnaphthalene,[41] 0.78 g (6.4 mmol) of crude sodium thiophenoxide, 20 mg of *o*-phenylenebis[diphenylphosphino]-nickel(II) bromide,[42] and 2 mL of ethylene glycol to give after workup 0.78 g (49%) of **2d**: bp 186−190°C/0.4 mmHg; ^{1}H NMR 7.91(dd, 1H, J = 7.5 Hz, J = 2.0 Hz), 7.70(dd, 1H, J = 7.5 Hz, J = 2.0 Hz), 7.69(s, 1H), 7.46(m, 2H), 7.34(s, 1H), 7.2−7.4(m, 5H), 2.60(s, 3H, CH_3); ^{13}C NMR 136.1, 135.6, 134.0, 132.3, 131.7, 130.7(×2), 129.3, 129.2(×2), 128.6, 128.1, 126.9, 126.3, 126.1, 124.1, 19.2; MS 250(M^+, 100), 249(14), 235(13), 234-(18), 217(13), 215(5), 202(11), 171(16), 141(15), 139(22), 129-(3), 117(8), 115(16). Anal. Calcd for $C_{17}H_{14}S$: C, 81.6; H, 5.7. Found: C, 81.5; H, 5.9.

1-Methyl-2-thiophenylnaphthalene (2f). A solution of 2 g (11 mmol) of 1-methyl-2-nitronaphthahlene[43] in 100 mL of 95% ethanol was hydrogenated in a Parr apparatus with 0.2 g of 5% Pd(C) at room temperature and 25 psi. Removal of the catalyst and solvent gave a solid residue, which was crystallized from petroleum ether (bp 35−60°C) to afford 1.6 g (93%) of 1-methyl-2-naphthylamine: mp 51°C (lit.[44] 50−51 °C); ^{1}H NMR 7.84(d, 1H, J = 8.6 Hz), 7.68(d, 1H, J = 8.1 Hz), 7.53(d, 1H, J = 8.7 Hz), 7.43(m, 1H), 7.23(m, 1H), 6.90(d, 1H, J = 8.7 Hz), 2.35(s, 3H, CH_3); ^{13}C NMR 141.1, 133.6, 128.5, 128.4, 127.0, 126.1, 122.4, 121.9, 118.3, 112.7, 11.5; MS 157-(M^+, 100), 156(82), 129(20), 128(27), 127(16).

A solution of 1.57 g (10 mmol) of 1-methyl-2-naphthylamine in 2 mL of acetonitrile was added over 10 min to a magnetically stirred mixture of 2.68 g (12 mmol) of CuBr, 1.76 g of isoamyl nitrite, and 40 mL of freshly distilled acetonitrile. The mixture was stirred for 30 min and poured into 200 mL of 20% HCl, which was extracted with 2 × 100 mL of ether. The combined ether extracts were washed with 2 × 100 mL of 20% HCl, dried over $MgSO_4$, and concentrated to an oily reddish residue, which was passed through column of 25 g of silica gel using hexane as the eluent. The solvent was removed and the residue vacuum distilled to give a fraction boiling at 119°C/0.25 mmHg; 2-bromo-1-methylnaphthalene 0.66 g (30%): ^{1}H NMR 7.98 (d, 1H, J = 8.7 Hz), 7.74 (d, 1H, J = 7.3 Hz), 7.56 (d, 1H, J = 8.8 Hz), 7.44−7.54 (m, 3H), 2.74 (s, 3H, CH_3); ^{13}C NMR 133.4, 133.3, 132.4, 130.0, 128.5, 127.4, 126.7, 125.7, 124.3, 122.7, 18.7; MS 222(M^+, 30), 220(33), 142(11), 141(100), 140(20), 139-(39), 115(48).

A mixture of 1.0 g (4.5 mmol) of 2-bromo-1-methylnaphthalene, 0.67 g (5.5 mmol) of crude sodium thiophenoxide prepared from thiophenol and NaH, 20 mg of *o*-phenylenebis[diphenylphosphino]nickel(II) bromide,[42] and 2 mL of ethylene glycol was placed in a 2 mm thick-wall glass tube (30 cm × 12 mm i.d.), solidified in liquid nitrogen, sealed under vacuum (0.25 mmHg), and heated at 200 °C for 24 h. The tube was cooled to room temperature and then in liquid nitrogen and opened, and the contents were poured into a mixture of 10 mL of CH_2Cl_2 and 60 mL of ether. The solution was washed with 4 × 50 mL of water, dried ($MgSO_4$), and concentrated to afford 1.05 g of an oily residue, which was chromatographed on 25 g of

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silica gel with 10% acetone in hexane to give, after short path distillation, 0.44 g (32%) of 1-methyl-2-thiophenylnaphthalene (**2f**): bp 190°C/0.8 mmHg; ^{1}H NMR 8.07(d, 1H, J = 8.6 Hz), 7.81(d, 1H, J = 8.8 Hz), 7.63(d, 1H, J = 8.6 Hz), 7.52(m, 2H), 7.43(d, 1H, J = 8.6 Hz), 7.22(m, 5H), 2.84(s, 3H, CH_3); ^{13}C NMR 137.2, 137.0, 133.11, 133.06, 130.9, 130.5, 129.1(x3), 128.5, 127.5, 126.9, 126.4, 126.0(×2), 124.6, 16.5; MS 250(M^+, 100), 235(9), 234(6), 215(5), 202(1), 171(20), 141(46), 140(10), 139(33), 129(6), 128(11), 117(9), 115(34). Anal. Calcd for $C_{17}H_{14}S$: C, 81.6; H, 5.7. Found: C, 81.7; H, 5.7.

Acknowledgment. This research was supported by grants from the T. C. U. Research Foundation and The Robert A. Welch Foundation.

JO0265176